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CHEMICAL TREATMENT OF PLATING WASTE FOR REMOVAL OF HEAVY METALS

John J. Martin, Jr.

Beaton and Corbin Manufacturing Company

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CHEMICAL TREATMENT OF PLATING WASTE FOR REMOVAL OF HEAVY METALS

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ABSTRACT

Chemical rinsing of electroplated parts and batch chemical treatment of spent processing solutions have been demonstrated to be a practical approach for abating pollution at a small captive metal finishing facility. The treatment system reduced the amount of chromium, nickel, zinc, copper and other heavy metals in the waste to a level where substantial quantities of water could be reused.

The precipitation of toxic metals in the chemical rinsing system produced an easily settled dense sludge, which was further compacted in simple outdoor earthen sludge beds for ultimate disposal as landfill.

This report was submitted in fulfillment of Grant No. 12010 DMF between the Industrial Pollution Control Section, ORM of the Environmental Protection Agency and the Beaton & Corbin Manufacturing Company.

Key Words: Chemical rinses, Electroplating Wastes, Chromium Treatment, Acid Nickel Treatment, Brass Bright Dip Treatment, Rinse Water Reuse.

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SECTION I

CONCLUSIONS

1. Discharge of spent processing solutions and dragout on the work and work carriers in electroplating operations introduces toxic metal ions into the rinse waters and causes pollution in streams and waterways.

2. Practical and economical treatment methods are necessary so that the small metal finishing facility is technically and financially capable of installing and operating an effective waste treatment system.

3. The use of chemical rinsing of dragout contamination from parts and batch chemical treatment of spent processing solutions provide a practical treatment approach for abating pollution at a small electroplating shop.

4. The waste treatment system produces an effluent containing less than 0.1 Cr (hexa), 0.5 Cu, 1.0 Ni, 0.5 Zn, and 5.0 suspended solids (all expressed in mg/l), which complies with the requirements of the authorities for stream discharge.

5. The type of equipment involved takes up relatively little space, is familiar to electroplating and plant maintenance departments and does not require special maintenance skills or procedures.

6. Control of the treatment processes can be readily assumed by the electroplater and does not call for special technical skills.

7. The effectiveness of chemical rinsing, which reduces the amount of rinse water required and permits substantial quantities to be reused, has resulted in about a 75% reduction in normal rinse water volume from 90 gpm to 20 gpm.

8. A simple blow-down, or bleed-off, of about 25% of the total water used keeps the dissolved salts at levels low enough to provide adequate rinsing at selected areas.

9. Chemical rinsing is not related to the volume of rinse water used and, therefore, wide variations in flow have no effect on the efficiency of the treatment.

10. Chromium was removed from the effluent as a dense hydroxide precipitate at a chemical cost of 38.8¢ per pound of chromic acid.

11. Acids were neutralized and the soluble metals precipitated as dense, readily settleable hydroxides at an annual cost of $810.30.

12. Sludge volumes are greatly reduced since the metals are precipitated as relatively dense hydroxides. In one year, the treatment of approximately 2200 pounds of chromic acid and 10,000 pounds of other acids resulted in about 100 cubic feet of sludge.

13. Treatment costs have not materially affected the competitive position of the company in marketing.

SECTION II

RECOMMENDATIONS

The program was limited to demonstrating that a suitable waste treatment system could be developed for the small captive type electroplating department. Such a system should be within the technical capacity of the plant personnel to operate and the effluent should be of a character acceptable to the authorities for stream discharge. The capital and operating costs should be within the economic capability of the company.

The technical and economic feasibility of automatic controls on the treatment wash solutions should be investigated and weighed against the present manual control.

Sumps for collecting and returning treatment wash solutions to the reservoir tank should be of larger capacity. At times all of the available volume of solution in the sump can be pumped to the reservoir tank before the level in the reservoir tank has risen above the overflow and returns the solution to the wash station. It is necessary to have a head over the overflow to insure good circulation, but if too much exists, on shut-down the reservoir drains to the wash station and thence to the sump and overflows the sump. Increasing the size of the sump from 30 gallons to 80, or 100 gallons would minimize this problem.

A monthly record of process and treatment chemicals used should be maintained. Such a record would be a further check on proper treatment.

Water flow rates should be monitored and logged monthly. Any significant variation would indicate some defect or malfunction in the system which can then be promptly investigated.

SECTION III

INTRODUCTION

The Beaton & Corbin Company was organized in 1893 to manufacture a then patented specialty in the heating field, namely the split floor and ceiling plates used where pipe passes through floors and ceilings to cover the gap between the hole and the pipe and present a pleasing appearance. Originally cast iron, these parts are now made of fabricated steel, assembled and electroplated by the company.

New products were inevitably added and for many years the company has been bending and forming tubular parts for a line of plumbers' brass goods. The line includes sink traps, waste bends, funnels, sink tailpieces, sink plugs, slip joint elbows, shower rods and water closet combinations. The majority of these items are electroplated.

The electroplating processes require the use of acids containing heavy metal ions, alkalies and large volumes of rinse water. Dragout on the work and work carriers into rinse waters and the periodic discharge of spent processing solutions are responsible for the pollution problem at the plant.

The plant is located in the Quinnipiac River Watershed area, and the effluent discharges directly to the Quinnipiac River which is a very small brook at this location.

On October 16, 1967, the Connecticut Water Resources Commission issued Order Number 479 directing that the company install adequate facilities to treat all water-borne industrial wastes so that they would be acceptable for discharge to the nearby receiving water.

Figure 1 shows the site arrangement and finishing department. Two areas appeared ideal for treatment equipment and sludge drying beds, provided the whole facility could be kept to a reasonable size. The finishing operations generated about 90 gpm of contaminated rinse water under full operating conditions, but contained only a small amount of contamination. If the pollutants could be kept out of the rinse water, the treatment could be confined to more reasonable volumes.

The company is representative of over three thousand similar sources of stream pollution in the New England area alone. If a system of chemical rinsing could be economically applied to produce a satisfactory effluent for discharge

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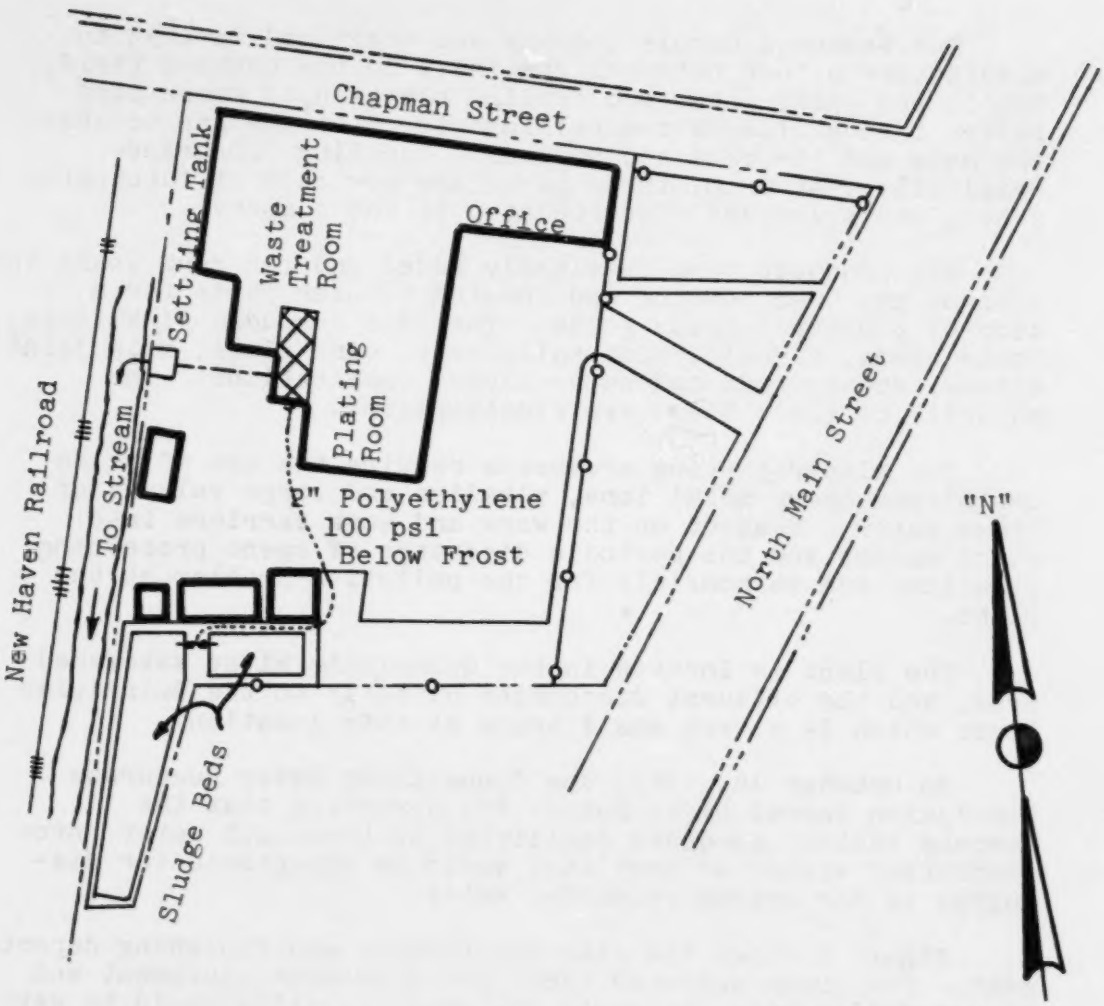

Figure 1. SITE PLAN

or reuse, it would be of significant value to many other firms facing similar orders to install treatment facilities.

A demonstration grant was obtained to install and demonstrate the use of a chemical rinsing system as an effective waste treatment method and to provide technical and economic data on the system.

The processing systems at the plant include alkali cleaners, weak and strong acids, acid nickel plating, chromium plating and bright dipping of copper alloys. At very infrequent intervals, a strong cyanide nickel strip solution is used on a few 10 in. x 10 in. baskets of parts. This might be four or five days a year with one or two baskets stripped per day.

All rinse waters and spent processing solutions were discharged to the floor where one drain line conveyed the effluent through a settling tank and thence to the stream. A larger filter was used occasionally to remove impurities from the nickel plating bath and this was backwashed to the floor and the cake washed away with the rinse waters.

If suitable chemical rinses could be provided in the process lines and were effective in eliminating toxic chromic acid and heavy metals, then the rinse waters should be suitable for discharge without further treatment. It would, of course, be necessary to pipe them to the stream so that floor spills would not contribute contaminants. Spent process solutions could be collected and treated as a batch. This was the basic approach for the design of the treatment facility.

The methods of treatment for each type of pollutant or category of pollutant are discussed in the following paragraphs.

In Figure 2, the method for treating spent processing solutions is shown. Spent alkalies are collected and batch treated with spent acids.

Spent acids are collected and batch treated with spent alkalies, or liquid caustic.

Spent cyanides are collected and batch treated with sodium hydroxide and sodium hypochlorite.

Floor spills are collected and batch treated as required for cyanide with sodium hypochlorite and for chromic acid with sodium bisulfite. The pH can be adjusted with sodium hydroxide or spent acids, as necessary.

In Figure 3, the treatment to remove nickel is shown. Dragout from the nickel plating bath enters a chemical rinse

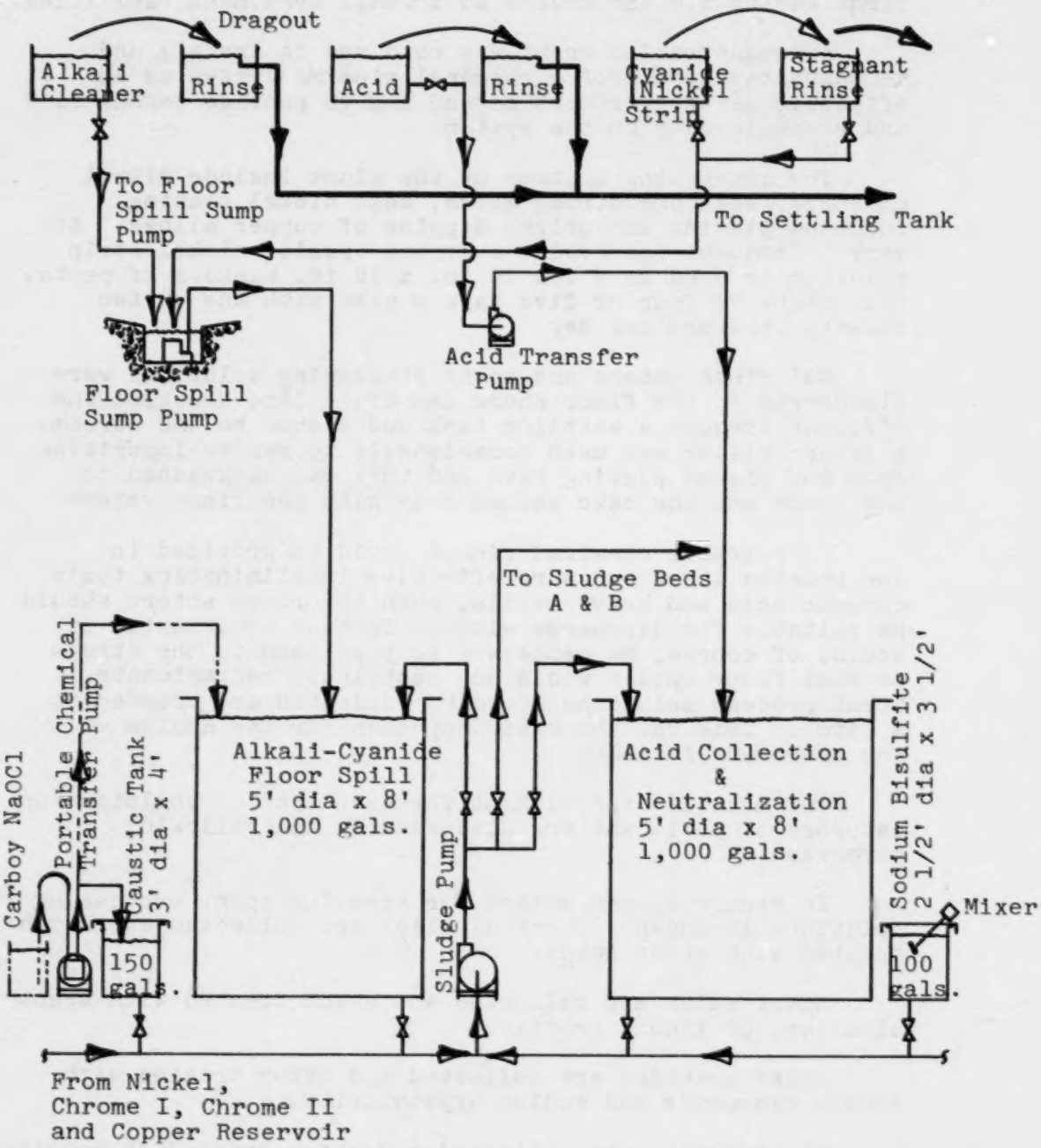

Figure 2. Alkali, Cyanide, Floor Spill, Acid Collect & Neutralize Flow Diagram

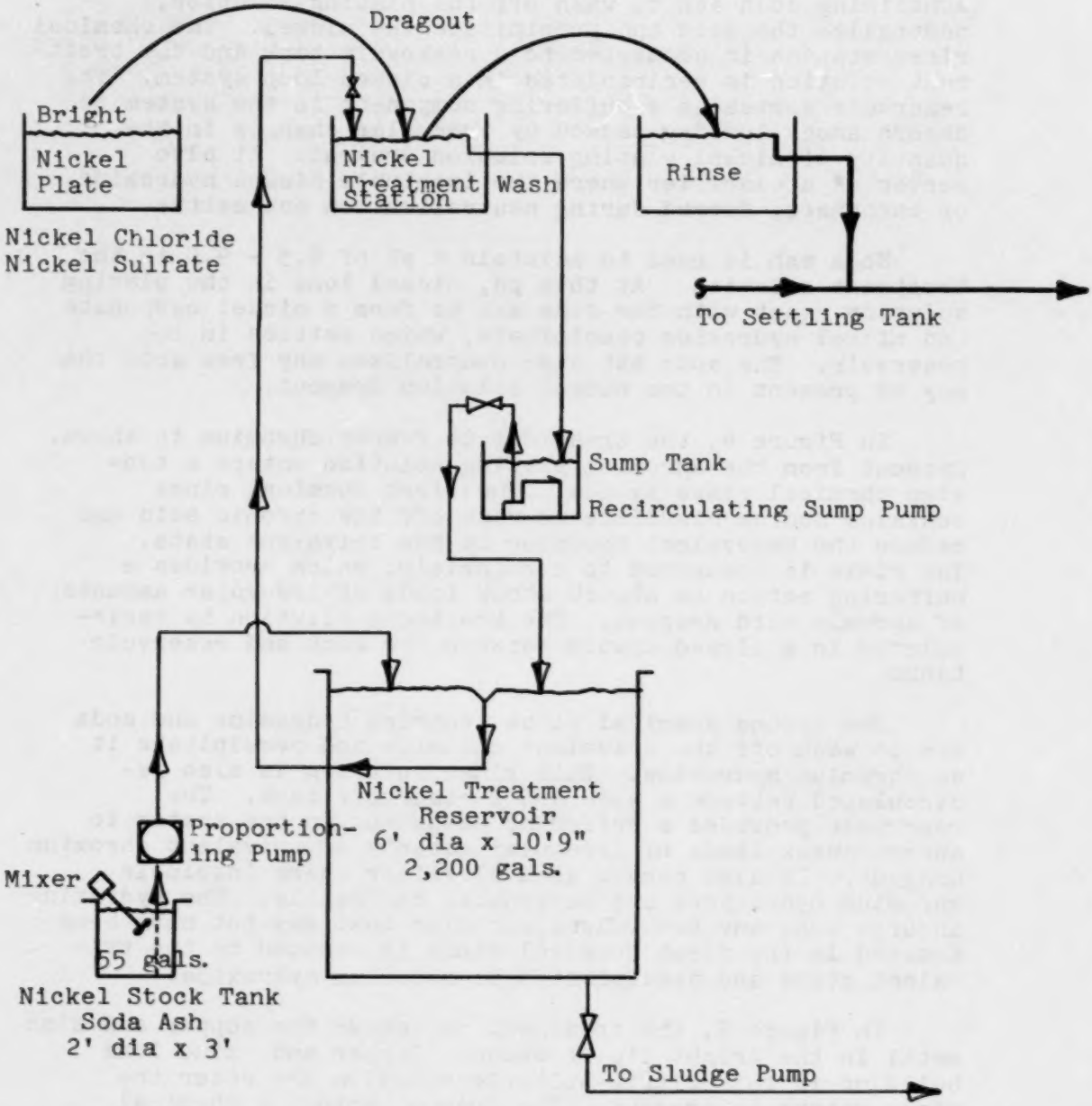

Figure 3. Integrated Nickel Treatment Flow Diagram

containing soda ash to wash off the plating solution, neutralize the acid and precipitate the nickel. The chemical rinse station is connected to a reservoir tank and the treatment solution is recirculated in a closed loop system. The reservoir serves as a buffering component in the system to absorb shock loading caused by irregular changes in the quantity of nickel plating solution dragout. It also serves as a clarifier where the insoluble nickel hydroxide, or carbonate, formed during neutralization can settle.

Soda ash is used to maintain a pH of 8.5 - 9.5 in the treatment solution. At this pH, nickel ions in the plating solution react with the soda ash to form a nickel carbonate and nickel hydroxide precipitate, which settles in the reservoir. The soda ash also neutralizes any free acid that may be present in the nickel solution dragout.

In Figure 4, the treatment to remove chromium is shown. Dragout from the chromium plating solution enters a two-step chemical rinse system. The first chemical rinse contains sodium bisulfite to wash off the chromic acid and reduce the hexavalent chromium to the trivalent state. The rinse is connected to a reservoir, which provides a buffering action to absorb shock loads of irregular amounts of chromic acid dragout. The treatment solution is recirculated in a closed system between the wash and reservoir tanks.

The second chemical rinse contains hydrazine and soda ash to wash off the trivalent chromium and precipitate it as chromium hydroxide. This rinse solution is also recirculated between a wash and a reservoir tank. The reservoir provides a buffering component in the system to absorb shock loads of irregular amounts of trivalent chromium dragout. It also serves as a clarifier where insoluble chromium hydroxides and carbonates can settle. The hydrazine insures that any hexavalent chromium that may not have been treated in the first chemical rinse is reduced to the trivalent state and precipitated as chromium hydroxide.

In Figure 5, the treatment to remove the copper and zinc metal in the bright dip is shown. Copper and zinc ions build up in this nitric-sulfuric solution and enter the rinse waters as dragout. The dragout enters a chemical rinse containing hydrazine, soda ash and caustic to wash the dragout from the work. The rinse station is connected to a reservoir through which the treatment solution is recirculated. The pH is maintained between 9.5 and 10.5 and the hydrazine concentration between 300 and 700 ppm. The caustic soda and soda ash neutralize the acid dragout and the hydrazine reduces the copper ions to the cuprous state. At the pH involved, cuprous hydroxide is precipitated. The reservoir acts as a buffering component to absorb shock loads due to irregular amounts of dragout and as a clarifier

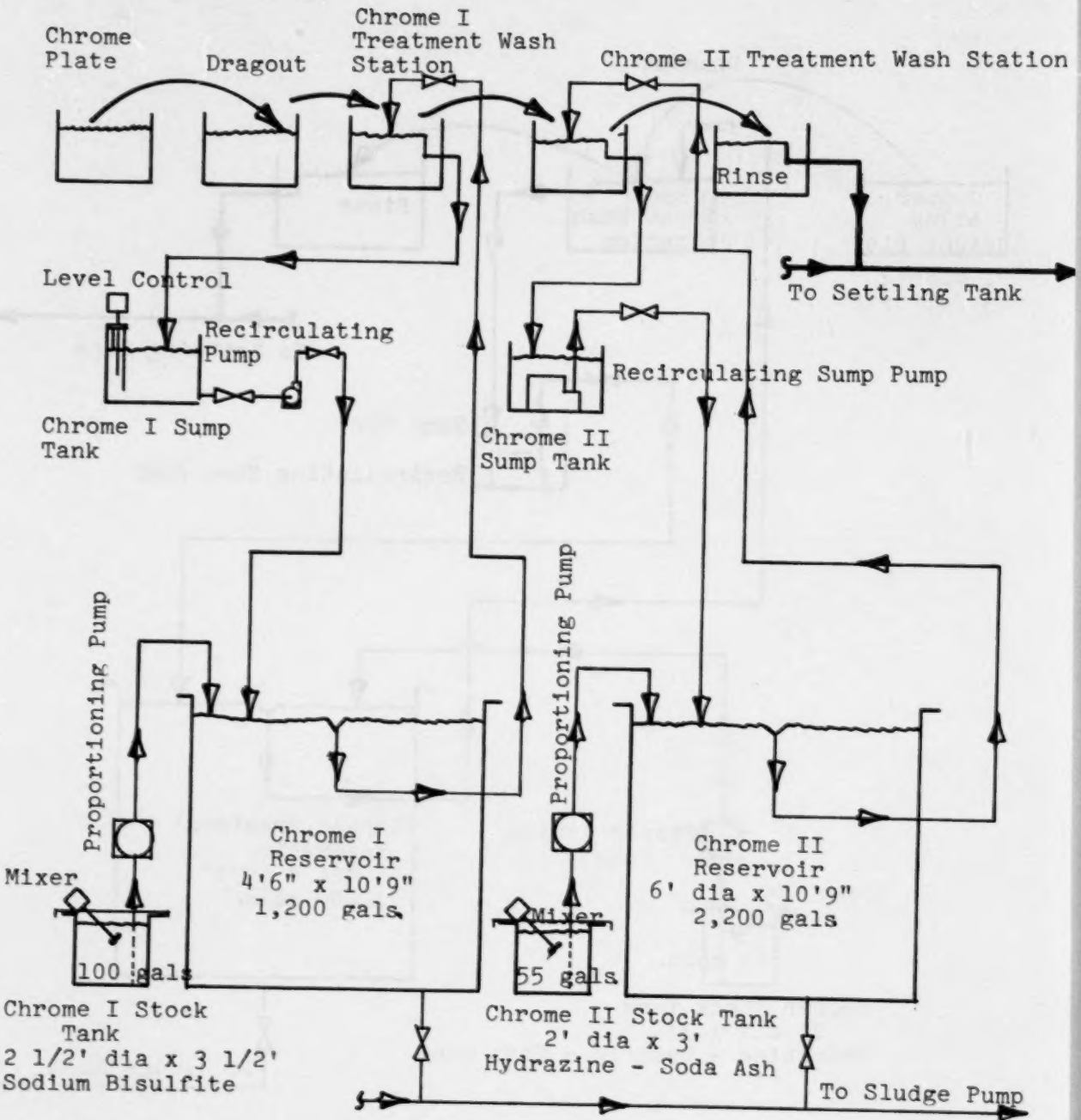

Figure 4. Integrated Chrome I & Chrome II Flow Diagram

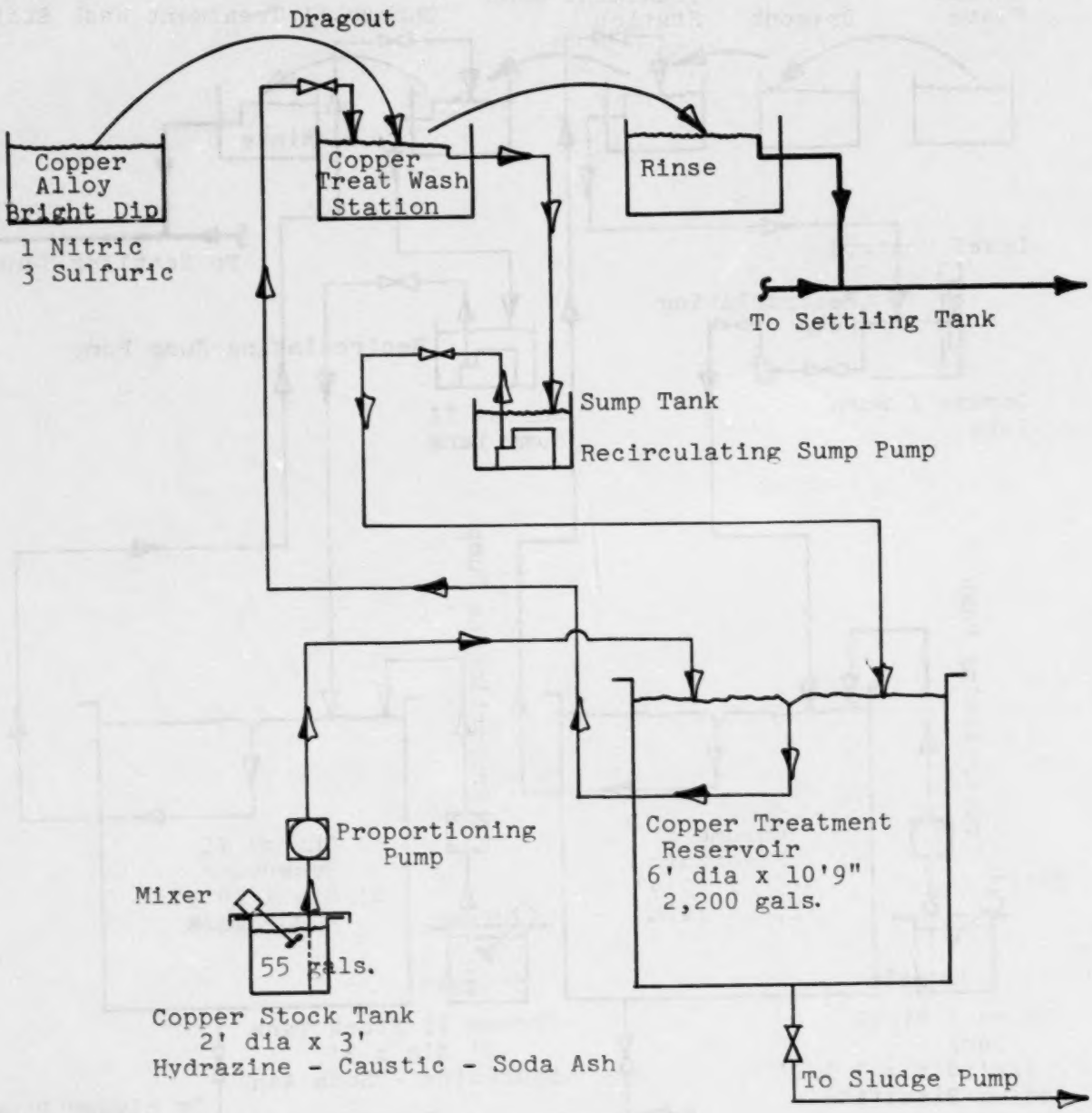

Figure 5. Integrated Copper Treatment Flow Diagram

where precipitated metal hydroxides can settle.

All rinse waters are piped to an existing settling tank where any remaining suspended solids settle and the clarified water is then discharged to the stream as shown in Figure 6. Since all spent processing solutions and floor spills are collected, contamination of the rinse waters from these sources are eliminated. Toxic dragout on the work and work carriers has been removed by chemical rinsing, eliminating this source of pollution in the rinse waters. Thus, only dragout from mild alkali cleaners, mild acid, and chemical rinses enter the rinse waters. Therefore, the rinse waters, with simple clarification, should be suitable for discharge to the receiving water or reuse for specific rinsing.

The chemical treatments result in the formation of precipitated metal hydroxides. The entire volume after batch treatment and periodic blow-down of the reservoirs is pumped to outdoor sludge beds, as shown in Figure 6, for compacting and drying. The compacted sludge, consisting primarily of inert metal hydroxides and oxides, will eventually be removed and used as landfill.

If the quantities of metals were large, the chromium and nickel precipitates could be salvaged by keeping them separate.

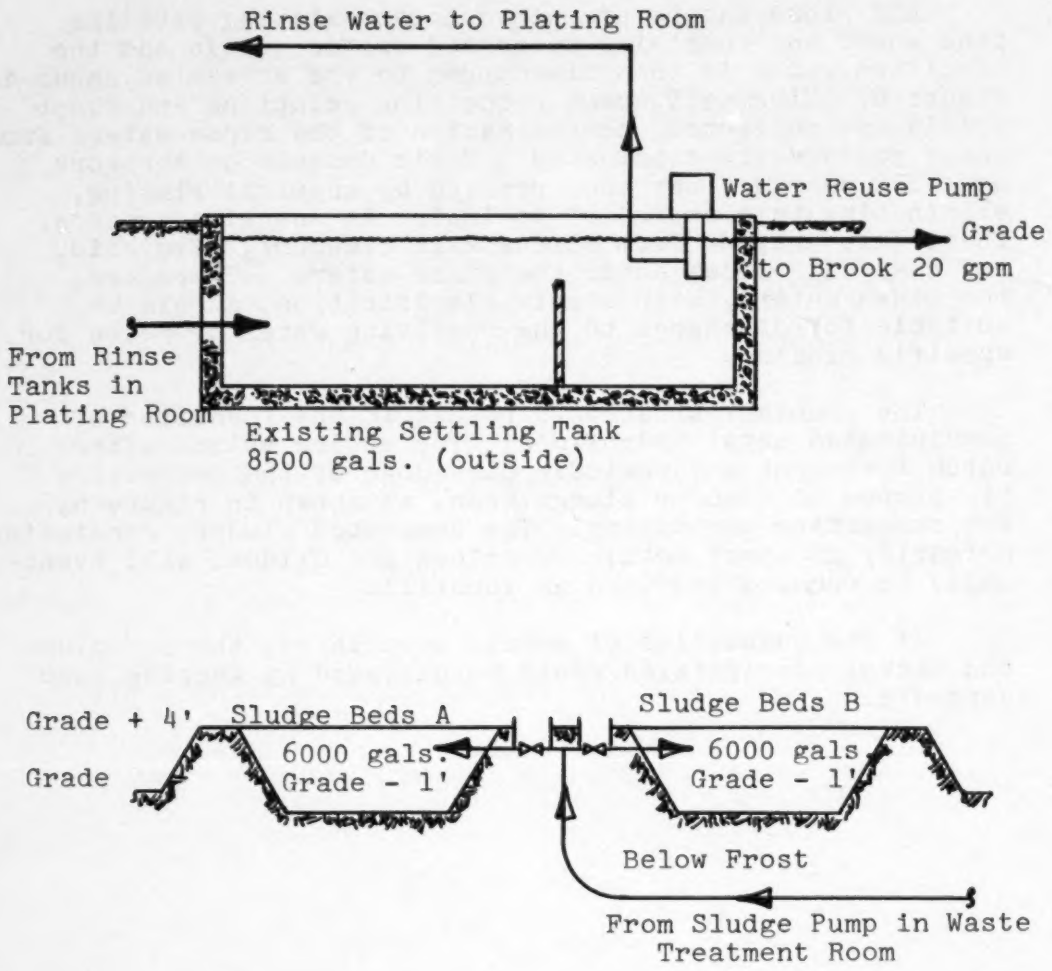

Figure 6. Settling Tank & Sludge Beds

SECTION IV

CONSTRUCTION

The finishing department can be considered to consist of three areas:

1. The Automatic Nickel-Chromium Plating Machine.
2. The Manual Tube Chromium Plating Line.
3. The Manual Bright Dip Line.

The dumpings of spent alkali cleaners (6-8 ounces per gallon) from these areas varies, but averages about 900 gallons every three weeks, with a maximum dump of about 300 gallons. A cyanide nickel strip with about 1 pound per gallon of cyanide is dumped about every three months and amounts to about 40 gallons. Floor spills should be negligible in the future except for occasional wash down which should not be more than 300 gallons. Considering these volumes, a 1000 gallon Alkali-Cyanide Floor Spill tank was selected.

The dumpings of spent acid amount to approximately 700 gallons about four times per year with a maximum dump of 300 gallons. This volume indicated that a 1000 gallon acid collecting and neutralizing tank should be adequate.

The sizes selected would allow the operator to batch treat approximately once per week. Thus, the operator would not be required to treat every time a spent processing solution was discharged, but rather at his convenience. It was recognized that the possibility of acid and cyanide meeting in the Floor Spill tank did exist. However, there will always be at least 90 gallons of alkali cleaner in the bottom of the Floor Spill tank, since the side drain does not permit emptying the tank completely, and this alkalinity, or that left from a batch treatment, should be effective in neutralizing any floor spill acid that might enter the tank. In addition, the use of cyanide is very infrequent and by treating batches when discarded the potential hazard is further minimized. Perhaps most important, however, is the presence of good ventilation in the plating department and the long experience of plating personnel in working with dangerous chemicals.

A sludge pump common to both tanks is used to agitate the solutions when batch treating and to draw in either liquid caustic or sodium hypochlorite, as required. If necessary, sulfuric acid could be added to the neutralizing tank from carboys with a self-priming chemical transfer pump, rated at 9 gpm.

A caustic stock solution tank of 150 gallons capacity was selected to hold a 30% solution of caustic. A spent acid solution of 300 gallons could contain 150 pounds of acid (6-8 ounces per gallons) and would require about 150 pounds of caustic. A 100 gallon solution of 30% caustic contains 333 pounds of caustic. Thus, a 150 gallon stock tank is suitable.

A sodium hypochlorite stock tank of 55 gallons was selected so that 15% liquid sodium hypochlorite could be transferred with the chemical transfer pump from 30 gallon carboys or 55 gallon drums. The sludge pump is then used to introduce the sodium hypochlorite when cyanide is treated.

After a batch is treated, the sludge pump is used to discharge the batch to the outdoor sludge beds. The sludge pump is also used to pump slugs of precipitated and settled metal hydroxides from the Chemical Rinse Reservoirs to the collecting tanks for treatment with spent processing solutions and thence to the sludge beds. The pump selected has a capacity of 40 gpm at a 70 foot head. Thus, a tank could be pumped to the sludge beds in about 25 minutes.

The existing drain in the floor was sealed off so that floor spill could not be discharged to the stream. A small sump, 12 in. by 12 in, by 18 in. deep, was constructed next to the former floor drain and a small self-operating submersible floor pump installed and piped to the Floor Spill tank. The floor could now be used to collect spent alkali and cyanide solutions and convey them automatically to the Floor Spill tank.

To collect spent acid solutions, a portable self-priming pump is connected to the nearest of two stainless steel quick disconnects which are piped to the Acid Collecting tank. The pump is rated at 9 gpm and about 35 minutes is required to empty the largest acid tank.

Since the floor is now contained, any drippage between tanks, tank overflows, accidental spill, or backwash of the nickel solution filter is prevented from going to the stream and is automatically transferred to the Floor Spill tank where it can be tested and appropriately treated.

All rinse tanks are permanently piped to the existing drain from which the effluent flows to the existing retention tank and thence to the river.

The Automatic Nickel Chromium Plating machine could have presented the most problems in applying chemical rinses because the addition of rinse stations could have been difficult, if not impractical. Figure 7 shows the existing stations and how they were converted to chemical rinse stations; no additional stations were required.

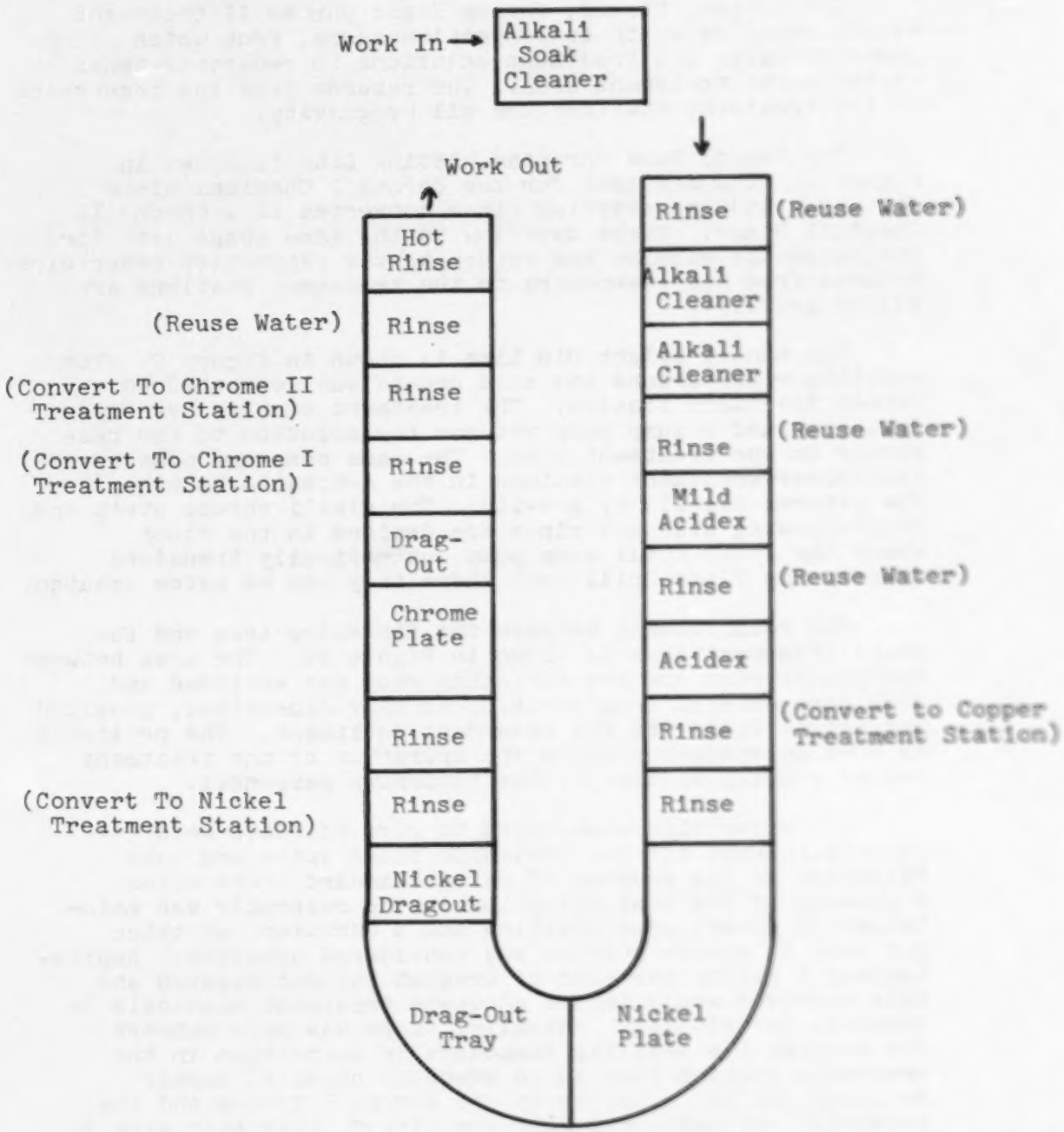

Figure 7. Automatic Nickel Chromium Plating Machine

The Copper, Nickel, Chrome I and Chrome II treatment washes overflow to their respective sumps, from which pumps transfer the treatment solutions to reservoir tanks in the waste treatment area. The returns from the reservoirs to the treatment stations are all by gravity.

The Manual Tube Chromium Plating Line is shown in Figure 8. One new tank for the Chrome I Chemical Rinse was added and one existing rinse converted to a Chrome II Chemical Rinse. These overflow to the same sumps used for the automatic machine and return to the respective reservoirs. Returns from the reservoirs to the treatment stations are all by gravity.

The Manual Bright Dip Line is shown in Figure 9. The existing rinse around the acid crocks was converted to a Copper Treatment Station. The treatment station overflows to a sump and a sump pump returns the solution to the reservoir in the treatment area. The same sump and pump serve the copper treatment stations in the Automatic Machine. The returns are all by gravity. The alkali chrome strip and the following stagnant rinse are drained to the floor where the floor spill sump pump automatically transfers them to the Floor Spill tank where they can be batch treated.

The relationship between the finishing area and the waste treatment area is shown in Figure 10. The area between the boiler room and the finishing room was enclosed and, with some careful consideration to tank dimensions, provided sufficient space for the treatment equipment. The proximity is most advantageous since the operation of the treatment can be readily assumed by the finishing personnel.

The reservoirs were sized to give adequate head for gravity return, fit the available floor space and take advantage of the economy of using standard stock molds. A minimum of one hour retention in the reservoir was maintained to insure good settling and a turnover of twice per hour in a wash station was considered adequate. Approximately 1 gallon per hour of dragout was anticipated and this turnover would insure adequate treatment chemicals in chemical pre-rinsing. Actually, there was more concern for keeping the metallic compounds in suspension in the treatment station than in an adequate chemical supply. Settling was not a factor in the Chrome I system and the reservoir was made only half the size of those that were to function as clarifiers.

The stock solution tanks were sized with the following considerations:

Chrome I Treatment - About 40 pounds of bisulfite per week would be required to treat a dragout of 40 gallons per week of chromium plating solution. A standard 100 gallon molded polyethylene container was selected.

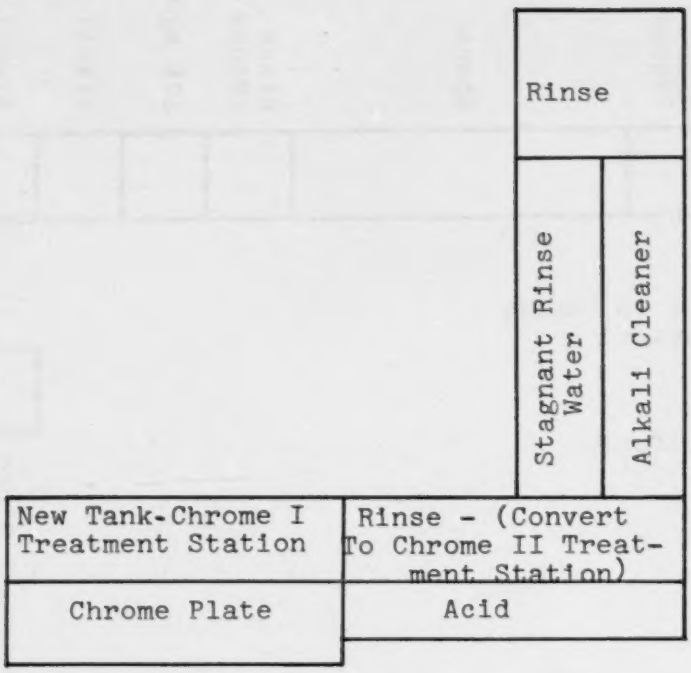

Figure 8. Manual Tube Chromium Plating Line

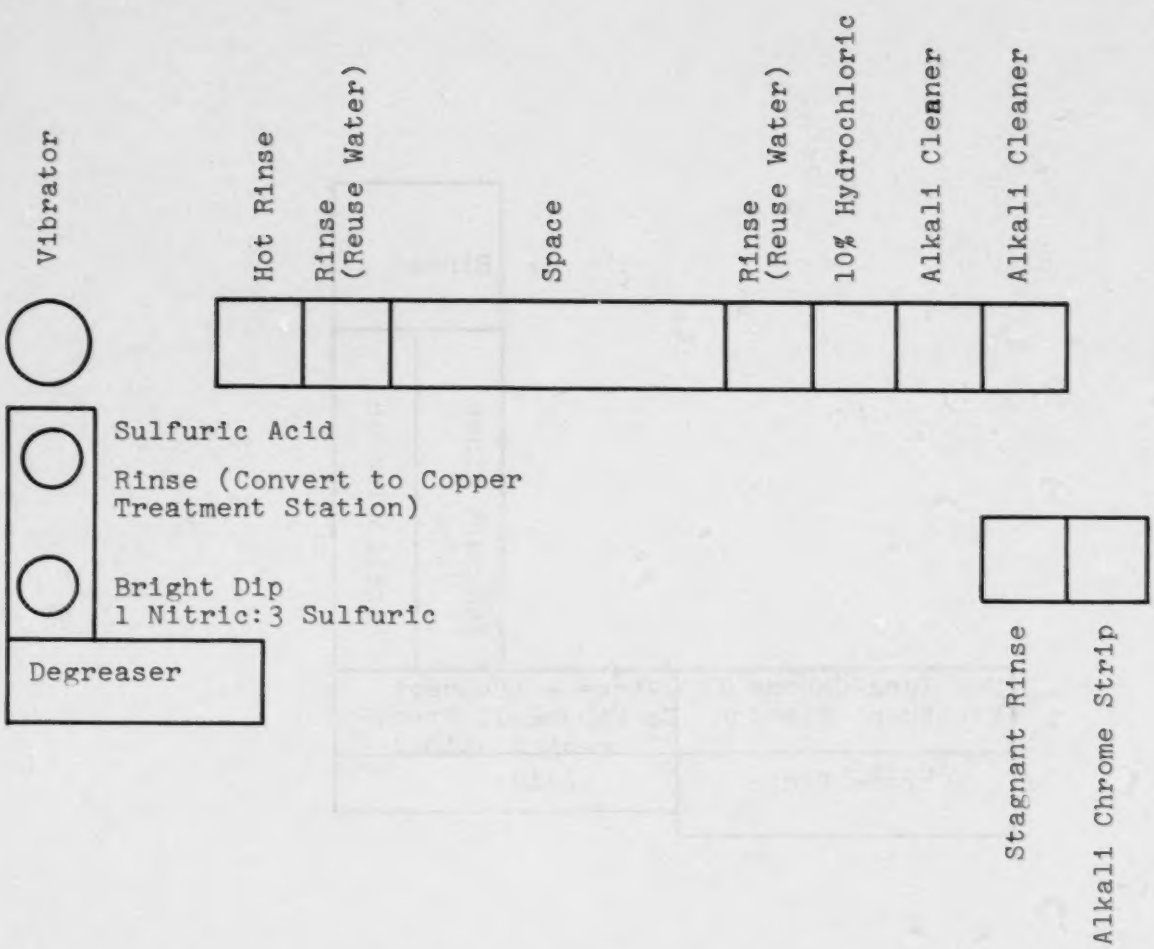

Figure 9. Manual Bright Dip Line

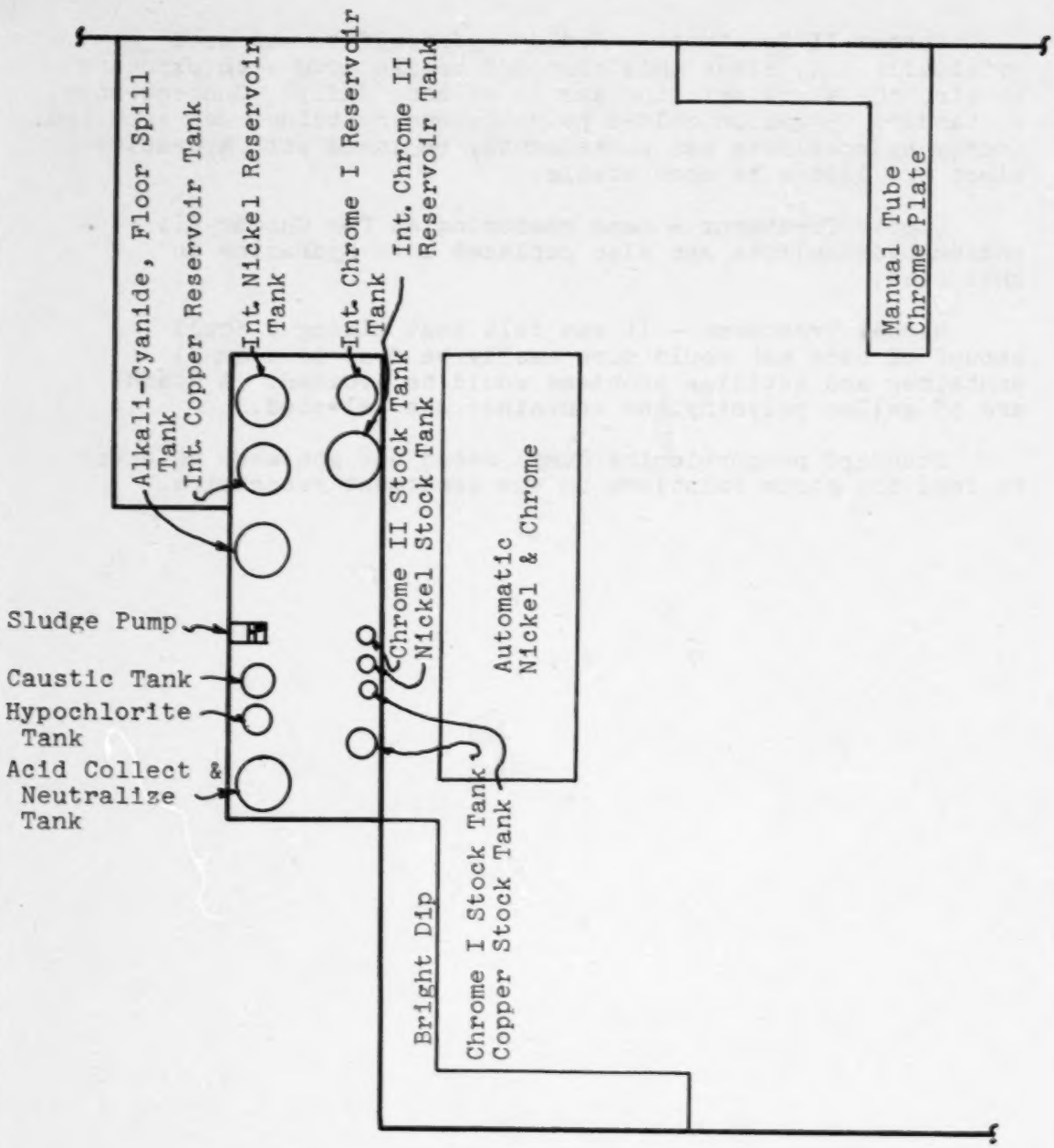

Figure 10. Plating and Treatment Areas

Chrome II Treatment - Sodium hydrosulfite was used originally and, since this compound breaks down with exposure to air, the stock solution was to be made daily. Consequently, a standard 55 gallon molded polyethylene container was selected. Sodium hydrosulfite was subsequently replaced with hydrazine since the latter is more stable.

Copper Treatment - Same reasoning as for Chrome II; sodium hydrosulfite was also replaced with hydrazine in this case.

Nickel Treatment - It was felt that mixing a small amount of soda ash could more easily be done in a small container and settling problems would be avoided. A standard 55 gallon polyethylene container was selected.

Standard proportioning pumps rated 0-8 gph were selected to feed the stock solutions to the treatment reservoirs.

SECTION V

OPERATION

The hydraulics of the installation are very simple. The sump pumps are started and the treatment solutions are pumped from the sumps to the reservoirs and then return by gravity to the treatment stations. With two stations and one sump, valves regulate the distribution to the treatment stations. Valves on the pump discharge regulate the flow rate.

Sumps having a capacity of 30 gallons were selected and are satisfactory, but a larger sump would allow more leeway in valve adjustment and accommodate surges on shut-down.

With all pumps running, the proportioning pumps are started with an arbitrary flow setting. Simple tests are provided to determine the chemical levels in the treatment solutions. Since the control limits are quite large, trial and error adjustments of the chemical feeds quickly result in settings which vary little from day to day. The varying level of chemical concentration does not result in poor treatment since an excess is all that is required for effective treatment.

The test procedures for the treatment solutions are as follows:

Chrome I Treatment

pH 2.5 - 4.5	narrow range pH paper, daily.
Sulfite 1000-2500 ppm	Spot test, daily, WCR-SOST, appended.
Solution color:	Bluish-green, no pink to brown.

Chrome II Treatment — Hydrazine used in place of sodium hydrosulfite.

pH 7.0-8.5	narrow range pH paper, daily.
Hydrazine 50-200 ppm	Spot test, every 4 hours, WNH-ST, appended.
Solution color:	Bluish-white, no yellow. WCR-NH_2 weekly.

Copper Treatment	Hydrazine used in place of sodium hydrosulfite.
pH 9.5-10.5	Narrow range pH paper every 4 hours.
Hydrazine 300-700 ppm	Spot test every 4 hours, WNH-ST, appended, WCR-NH_2 appended, weekly.
Nickel Treatment	
pH 8.5-9.5	Narrow range pH paper, daily.

SECTION VI

DISCUSSION

A summary of the effluent analysis is presented in Table 1. Since the dragout from the chemical treatment wash station into the rinse water would always be of an alkaline nature, no control was used to adjust the pH of the effluent. Thus, other than some minimal clarification in the existing retention tank, the running rinse water does not receive any treatment.

The effectiveness of the chemical treatment system is rather dramatically demonstrated by comparing the contamination before and after the treatment was instituted as shown in Table 1. In all areas the values obtained are well within the limits acceptable to the State for discharge to this stream.

It was anticipated that the effluent, after treatment was instituted, should be of value for further reuse. Since there would be a build-up of dissolved salts if all the water were reused, it was planned to use this water only where a slight amount of salt would have no deleterious effect on the process. The critical areas would continue to be supplied with fresh water to replace the bleed from the system and keep the dissolved salts at a low level. Thus, after alkali cleaners and acid dips, reuse water is used. It is not used in the rinse before nickel plating, chromium plating, as a final hot water rinse, or as make-up to processing solution.

At present, the discharge from the settling tank to the stream is running about 20 gpm. Five stations are on reuse water and three are on city potable water. About three quarters of the process water is reused in the process. Without this type of treatment, 90 gpm of rinse water would be used and discharged.

In Table 2, the actual process chemical and treatment chemical usage is presented. The caustic requirement was significantly lower than might be expected because of the neutralizing effect of the alkali cleaners.

To reduce and precipitate slightly less than 2200 lbs of purchased chromic acid required

2388	lbs of sodium bisulfite @	$267.60
550	lbs of hydrazine @	523.00
1000	lbs of soda ash @	60.00
	or a total of	$850.60

Table 1

Effluent Analysis

(mg/l)

		Chromium		Copper		Nickel		Zinc						
	pH	Hexa.	Total	Sol.	Total	Sol.	Total	Sol.	Total	S.S.	CN	Cl	SO_4	NO_3
Before Treatment														
6/30/65														
9-10	3.0	10	-	6	-	5.0	-	5.0	-	270	0.9	-	-	-
10-11 AM	3.1	12	-	8	-	5.0	-	2.0	-	280	1.0	-	-	-
11-12	2.7	14	-	8	-	3.0	-	3.0	-	304	0.9	-	-	-
3/18/65														
9-10 AM	2.2	8	12	15	-	7.0	-	3.3	-	404	1.0	-	-	-
10-11	2.3	9	14	13	-	6.5	-	3.3	-	380	0.6	-	-	-
11-12	2.3	9	12	11	-	5.5	-	2.6	-	400	0.5	-	-	-
12-1	2.3	10	14	11	-	5.5	-	3.3	-	368	0.5	-	-	-
8/24/66	2.8	20.5	24	15.5	-	14.2	-	-	-	836	6.8	-	-	-
State Limit														
	6.5-8.5	1.0	-	1.0	-	1.0	-	1.0	-	30	0.1	100	200	100
After Treatment (*ND - Not Detectable)														
10/16/70														
Composite	7.0	ND	ND	0.09	-	0.95	-	0.29	-	ND	ND	31.3	950	1.76
12/3/70														
Composite	7.15	ND	ND	0.20	0.30	0.20	0.40	0.34	0.39	1.70	-	19.0	130	0.20
12/16/70														
Composite	7.18	ND	0.025	0.25	0.45	0.60	0.60	0.44	0.50	2.3	ND	23.1	160	0.20

which is at the rate of 38.8¢/lb of chromic acid purchased.

To complete the neutralization of 10,000 lbs. of acid and 9375 lbs. of alkali cleaners required

2200 lbs. of sodium hydroxide	@	$ 71.30
200 lbs. of soda ash	@	10.00
		81.30

To precipitate the metals as dense hydroxides which can be settled readily and prevented from entering the effluent required

770 lbs. of hydrazine @	$729.00

which for acid-alkali neutralization, metal precipitation and settling is a total of $810.30

The hydrazine consumed in neutralization is that used in the Integrated Copper treatment to precipitate the copper as a heavy cuprous hydroxide which settles rapidly.

A summary of the operating and capital carrying costs is presented in Table 3. The labor and electrical costs are estimates, but the chemical and capital charges are actual.

Table 2

Chemical Consumption 1970

	Process, lbs	Treatment, lbs
Chromic Acid	2200	
Acid Salts	3075	
Sulfuric	4265	
Nitric	960	
Muriatic	1800	
Alkali Cleaners	9375	
Sodium Cyanide	30	
Sodium Bisulfite		2388
Soda Ash		1200
Hydrazine, 54.4%		1320
Sodium Hypochlorite, 15%		75 gals.
Wetting Agent		5 gals.
Caustic		2200

Table 3

Waste Treatment Costs

Chemical	lbs./yr	Price/lb.	
Sodium Bisulfite	288	$ 0.20	$ 57.60
Sodium Bisulfite	2100	.10	210.00
Soda Ash	700	.05	35.00
Soda Ash	500	.07	35.00
50% Liquid Caustic	155 gals.	.46/gal.	71.30
Hydrazine, 54.4%	1320	.95	1252.00
Sodium Hypochlorite, 15%	75 gals.	.68/gal.	51.00
Wetting Agent	5 gals.	4.60/gal.	23.00
Total Chemical Costs			$1734.90
Labor 480 hrs @ $ 5.00			2400.00
Power 6000 KWH @ .02/KWH (approx)			120.00
Total Operating Costs per year			4254.90

Building, Sludge Beds, Fencing, Heating, Exhaust, existing equipment changes, treatment equipment, plumbing, electrical and technical services----------$ 47,337.00

With 10 year depreciation----------$ 4733.00 per year

Carrying charges 6%---------- 2840.00

Amortization----------$ 7573.00 per year

Total Operating and Amortization Costs---$11828.00 per year

Table 4 shows the relationship of treatment costs to product area and dollar value. The area of the product is significant, as well as its shape, since both determine the amount of dragout that must be subsequently treated.

Table 4

Unit Waste Treatment Costs

Water volume----------11,450,000 gals./yr

Total Waste Treatment Cost----------$11,828.00 per year

Area of Processed Product----------660,000 sq ft/yr

Treatment cost per sq ft----------1.79¢/sq ft

Value added by Finishing----------$205,000.00/yr

% Waste Treatment Cost per value added----5.75%

Total Value of Processed Product--------$820,000.00/yr

% Waste Treatment Cost of Product Value--1.44%

Note:

The above treatment costs do not consider any savings resulting from water reuse.

SECTION VII

ACKNOWLEDGMENTS

The cooperation of the Connecticut Water Resources Commission in reviewing the plans, specifications and anticipated effluent quality is appreciated.

The construction and operation of the system was conducted under the direction of A. Ralston, C. Dutton and M. Adam of the Beaton and Corbin Company, which included coping with interruptions in production operations as the system was installed and the new procedures incorporated. The accumulation of the data for this report was also accomplished by this group.

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SECTION VIII

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SECTION IX

APPENDIX

Test Procedures:

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TEST PROCEDURE: WCR-SOST

TEST: APPROXIMATION OF EXCESS SULFITE RADICAL IN CHROMIC ACID TREATMENT SOLUTION I

1. Take a 100 ml sample of the solution and place in a 250 ml Erlenmeyer flask and heat to 140-160°F.

2. Place one drop of 2 N H_2SO_4 and one drop of Diphenylcarbazide Indicator in each of several cavities of a spot plate.

3. Using a stirring rod, place a drop of the solution on the spot plate so that it comes in contact with the indicator. The indicator will turn pink if CrO_3 is present, but remains green or the color of the treatment solution if excess $SO_3^{=}$ is still present.

4. From a burette, run in 5 ml of standard chromic acid solution (10 g/l). Again test a drop of the spot plate and repeat this process until the indicator turns pink to violet.

5. Calculations:

   Each 5 ml of chromic acid solution used indicates an excess of .8 g/l $SO_3^{=}$ content expressed as $NaHSO_3$.

Maintain the $SO_3^{=}$ concentration in the treatment solution so that at least 5 ml chromic acid is needed to yield the pink color. If more than 30 ml chromic acid is used, the excess $SO_3^{=}$ is high and the sodium bisulfite additions should be reduced. This would be equivalent to an $SO_3^{=}$ concentration of between 0.8-5 g/l for best performance.

TEST PROCEDURE: WNH-ST

TEST: Hydrazine Spot Test for Excess Hydrazine

SPECIFICATIONS:

Type----------Quantitative Approximation
Limit of Identification---------50 ppm N_2H_4
Color----------Pale Yellow

REAGENTS:

1. p-Dimethylaminobenzaldehyde - Dissolve 1 gram of p-Dimethylaminobenzaldehyde in methyl alcohol and dilute with methyl alcohol to 100 ml. This indicator is stable for several weeks if stored in a dark glass stoppered bottle.

2. Hydrochloric Acid Solution 10% by volume - to 50 ml of distilled water, add 10 ml of concentrated hydrochloric acid and dilute to 100 ml with distilled water.

PROCEDURE:

1. Place two droppers full (approximately 2 ml) of treatment solution to be analyzed in a 100 ml graduate and dilute to 100 ml with distilled water and shake to mix.

2. Place one drop of diluted treatment solution in one cavity of a spot plate. In another cavity, place one drop of distilled water for a blank.

3. To each spot add 2 drops of hydrochloric acid solution and mix.

4. Add 2 drops of p-Dimethylaminobenzaldehyde indicator and mix. Wait one minute for color development. The sample spot will turn very pale yellow if 50 ppm hydrazine is present. The yellow color will increase in intensity as the hydrazine concentration increases. At 700 ppm hydrazine, the spot will be very deep yellow. The blank should always remain colorless.

TEST PROCEDURE: $WCR\text{-}NH_2$

Test: Hydrazine Titration - 2

Specifications:

Type----------Quantitative

Color at End Point---------red to yellow or light orange

Reagents:

1. Amaranth Indicator Solution, 0.2%. Dissolve 200 mg in water and dilute to 100 ml.
2. Hydrochloric acid, conc.
3. Potassium iodate solution (0.025M). Dissolve 5.350 g KIO_3 in water and dilute to one liter.

Procedure:

1. Pipet a 5 ml sample of previously filtered treatment solution into a 250 ml Erlenmeyer flask.
2. Add 5 ml of conc. hydrochloric acid and mix.
3. Add 6 drops of Amaranth indicator solution.
4. Titrate, while shaking or stirring vigorously, with potassium iodate solution. The sample color will change from red to yellow or light orange.

Calculations:

$$\text{mg/liter (ppm) } N_2H_4 = \frac{\text{ml } KIO_3 \text{ used} \times 800}{\text{ml sample used}}$$